

pressures. This altered shock then interacts with the free surface imparting to it a velocity $2u'_{p2} > 2u_{p2}$. We have neglected thermal effects that tend to expand the lattice behind the shock again making $u'_{p2} > u_{p2}$.

Let us also consider the impedance technique of Larson. Following Larson, we will assume a linear relation between P and u_p in the low pressure region as shown in figure 7.

A shock of pressure P_Q in the quartz will be generated by a shock of pressure P_{Bi} striking the Bi-quartz boundary. A rarification wave of magnitude $P_{Bi} - P_Q$ will be reflected back into the Bi. Conserving pressure at the boundary and using equation (2) and figure 7 we find

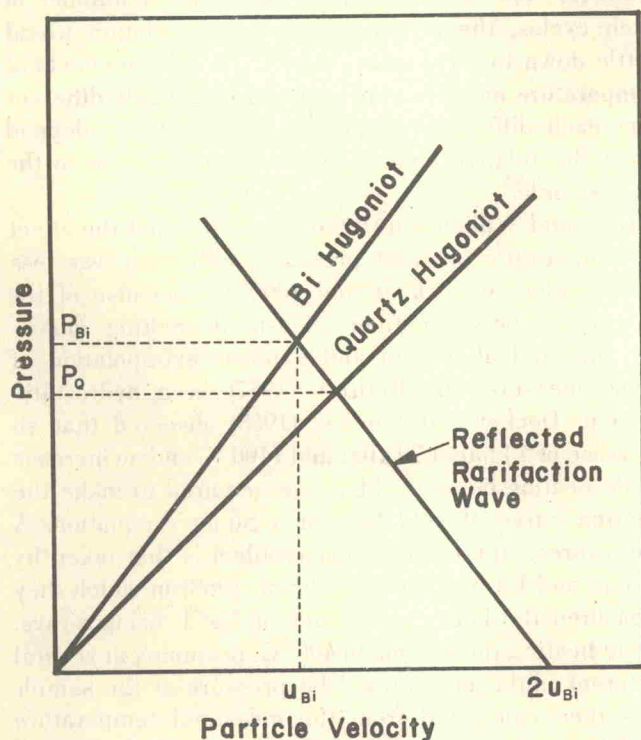


FIGURE 7. Pressure vs particle velocity curves for a Bi plate against a quartz crystal with the shock progressing from Bi into quartz.

$$P_{Bi} = \frac{(\rho_Q U_Q + \rho_{Bi} U_{Bi})}{2\rho_Q U_Q} P_Q \quad (13)$$

where ρ and U stand for the density behind the shock and shock velocity in the two media. For the elastic wave one would estimate the rarification wave returning into the Bi to be about 0.7 kbar. This wave interacts with the plastic wave lowering the pressure by this amount before it strikes the surface. Thus, the "measured" pressure in the plastic wave should be increased by 0.7 kbar.

The above correction would bring Larson's measurements into excellent agreement with the static work of Vanfleet (1967). In this hydrostatic measurement, Vanfleet observed transition rates for Bi I-II which show that if nuclei of the Bi II phase are present, the transition is very rapid for an overpressure of $1/2$ to 1 kbar.

It is quite possible that the shock wave will nucleate all possible phases and thus the only criterion for a rapid change of phase is to have enough excess pressure above the equilibrium value.

b. Transition in Iron

Another transition, measured in shock work, that might be useful for pressure calibration is the α - ϵ Fe transition above 100 kbar. This transition was measured as 130 kbar at 37 °C by Bancroft, et al. (1956). Corrected to the hydrostat, the pressure would be about 128 kbar. They also observed some effect of sample thickness indicating that the shock times are possibly shorter than or of the same magnitude as the transition time. Later measurements (Loree, et al., 1966) gave 127 ± 1 kbar after making the strength of material correction. These measurements assumed the free surface velocity was twice the particle velocity behind the shock. As discussed above, this may give a calculated pressure which is slightly high. The temperature dependence of this transition has been measured between 78 K and the α - γ - ϵ triple point, which has been set by shock data as 110–115 kbar and 500 °C (Johnson, et al. (1962)). These measurements could not accurately determine the absolute pressure and thus the pressures were adjusted to agree with the values of Bancroft, et al., for shock in iron at room temperature. The α - ϵ transition has been measured in static work by Balchan and Drickamer (1961) at 133 kbar but they used calibrants whose pressure was determined by shock data. However, this measurement shows not only that shock pressures agree with each other but also that transition pressures may not be greatly altered by the plastic shear strain in the shock front.

To conclude this section, we comment that it appears that one should be very cautious in using the pressures from shock measurements as calibration points for static measurements. The major problems are the strength of material corrections, which can be reasonably well approximated but have not always been included, and rate effects on transition pressures for which very little is known.

6. Pressure Scale at Elevated Temperatures

Many measurements have been made at elevated temperatures and high pressures. These include melting curve determinations, detection of solid-solid and other types of phase lines, chemical reactions, effects of temperature and pressure on electrical resistance, and diffusion measurements. With very few exceptions, the pressure in these experiments has been taken from a room temperature calibration of the apparatus. In a few cases, experimenters have tried to estimate the effects of elevated temperatures upon the pressure calibration. These estimates vary greatly. Bundy (1964) proposed a 16 kbar rise in pressure when internally

heating his pressure chamber to 500 °C at 100 kbar. Lees and Williamson (1965) conclude that the effect of temperature on the load/pressure calibration is less than 3 kbar at 50 kbar and 1000 °C. Decker and Vanfleet (1965) felt that the effects of temperature might depend strongly upon the nature of the gasket formation while Millet (1968) proposed that the pressure might even decrease when internally heating a specimen at pressures where the gaskets have not completely formed. Millet's argument centers around the relieving of pressure gradients at elevated temperatures.

Because of the difficult nature of this problem, very little definitive research has been done. With our present technology, however, it is possible to attack the problem. A few experiments have been reported which give preliminary answers to some of these questions. These experiments will be briefly discussed here. In that the effect may depend considerably upon the nature of the experimental apparatus, we will discuss each general type separately.

A problem which is related to that above is the effect of pressure upon the e.m.f. of thermocouples and their calibration. This problem will also be discussed in the present section and we will then conclude by mentioning some techniques which have been proposed to calibrate presses at elevated temperatures. In multianvil devices, the anvils are forced against the faces of a three dimensional pressure cell made of materials such as pyrophyllite or a thermo-setting plastic mixed with boron, etc. (Barnett and Hall, 1964). As the pressure cell is compressed, some of the material extrudes between the anvils forming gaskets. When the friction between the cell material and the anvils is sufficiently large, the flow of material in the gasket region ceases and the pressure within the cell rises as more load is applied. The gasket regions are also compressed as the load increases and eventually assume a large share of the total load, thus limiting the useful pressure at the center of the cell. Large pressure gradients will be present in the gaskets and much smaller pressure gradients are set up in the bulk of the pressure cell.

It is not practical to heat the entire apparatus because of its large mass. Neither is it desirable to do so, in that high temperatures would weaken the anvils, etc. Thus, the heating must be accomplished internally and the cell material must also serve as a good thermal insulator between the high temperature furnace region and the anvils, which will remain near room temperature.

As the temperature of the furnace region is increased, the heated material will expand against the colder surrounding material. This outer region, being composed of solid material, will resist the expansion until a sufficient pressure gradient is set up to force material outward. Thus, the pressure in the furnace area would be expected to increase. The new distribution of pressure through the solid medium pressure cell might cause more material to move into the gaskets and also possibly drive the anvils back, increasing the oil pressure

behind the rams. Another fact that complicates the problem is that the mechanical properties of the heated material may change, i.e., become less viscous, and relieve pressure gradients in the furnace region. Because of these latter effects, one cannot be certain as to whether the pressure at the sample monotonically increases with rising temperature or not.

Upon cooling the furnace area, the inner material will contract but will probably not return to the initial state prior to heating. The high temperature may also have irreversibly altered the nature of the cell material. Because of these two changes, the entire process may not be repeatable from one heating cycle to the next. However, one would suppose that after a number of such cycles, the pressure-temperature relation would settle down to a repeatable cycle. The above effects of temperature on the sample pressure are likely different for each different cell material and will also depend upon the relative volume of the furnace region to the total sample.

Lees and Williamson (1965) concluded that the effect of temperature on their pressure calibration was less than 3 kbar at 50 kbar and 1000 °C, because of the agreement between their measured melting curves for zinc and aluminum and a linear extrapolation of those measured by Butuzov (1957) in a hydrostatic system. Decker and Vanfleet (1965) observed that an increase of 4 kbar at 70 kbar and 1400 °C and no increase when heating below 15 kbar was required to make the melting curve of gold best fit a Simon's equation. A more direct approach to this problem is that taken by Young and Barnett (private comm. 1968) in which they measured the lattice parameter of NaCl, using x-rays, while heating the sample to 400 °C, beginning at several different initial pressures. The pressure at the sample was then calculated from the measured temperature and lattice parameter using Decker's (1971) equation of state. For a 50-50 boron-plastic tetrahedron with preformed gaskets and using $\frac{5}{16}$ " double tapered anvils, they found the pressure to increase with temperature but not monotonically. At 60 kbar and 400 °C their measured increase was about 4.5 kbar.

The basic principles of the belt and girdle apparatus are very similar to those of multianvil systems and thus we would expect similar effects of temperature on pressure. The principal differences would come from different geometries and thus also different pressure gradient patterns.

Bundy (1964) proposed a 16 kbar rise in pressure in a belt apparatus when heating to 500 °C near 100 kbar. His conclusion was reached by comparing the difference between the triple point of iron measured in his apparatus and that obtained by shock techniques. Bundy's Bi III-V point in these measurements was higher than that presently accepted. A 26 kbar increase would be required using more recent calibrations to bring his measurements into coincidence with the shock work. The problem here may stem from the inappro-